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Lemon aids green synthesis of reduced graphene oxide-based FET sensors for the detection of Lead and Cadmium ions in water

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***Abstract*— Graphene is the most fascinating material due to its exceptional electrical and mechanical properties. The reduced form of graphene oxide (GO) is best suitable for sensor applications. There are numerous methods available for reducing GO by synthetic reducing agents that are not environment-friendly and cost-effective. Therefore, in this research work, natural lemon juice is used as a potential reducing agent. It creates defects on the GO surface by altering various functional groups. These are clearly visible in Raman and FTIR results and help in the sensing of the lead (Pb^{2+}) and cadmium (Cd^{2+}) ions. Field effect transistor (FET) based active structure is used to amplify its sensitivity and discriminate the lead and cadmium ions by tuning the gate voltage. The optimized gate voltages for lead (Pb^{2+}) and cadmium (Cd^{2+}) ions are -1.6 V and 0.8 V, respectively, at which the sensor shows the maximum response. This green synthesis approach of sensor fabrication highlights sustainable and cost-effective solutions in the field of reduced graphene-based FET sensors.**

Keywords— *Graphene oxide (GO), Reduced graphene oxide via lemon (rGO-L), Green synthesis, Field Effect Transistor (FET), Selectivity.*

I. INTRODUCTION

Reduced graphene oxide (rGO) is an exceptionally beneficial material for future applications of nanotechnology-based sensors due to its electronic properties [1]. There are numerous methods available in the literature, such as micromechanical exfoliation of graphite [2], chemical vapor deposition [3], and solution-based chemical reduction of graphene oxide (GO) to graphene [4], have been developed. Among those methods that are notable is the solution-based chemical reduction of GO, which offers the benefits of cost-effectiveness and large-scale manufacturing. The chemically reduced graphene sheet is less soluble in water due to a strong π-π stacking tendency [5]. This is due to the presence of the capping reagents or surfactants used. On the other hand, these capping reagents or surfactants change the properties of the material. Additionally, the most successful reduction of graphene oxide (GO) was done with the help of hydrazine hydrate as the reducing agent [6]. However, hydrazine hydrate is highly poisonous and harmful to health and the environment. Therefore, a new approach to green synthesis was developed with the help of lemon juice in this work. Lemon juice is a naturally employed reducing agent, and it has mild reductive ability and nontoxic properties [7], [8], [9]. Lemon-reduced graphene oxide (rGO-L) was used as the sensing material for heavy metal ions, i.e. lead (Pb^{2+}) and cadmium (Cd^{2+}) [10]. Lead (Pb^{2+}) [11]and cadmium (Cd^{2+}) ions [12] are extremely harmful pollutants in the biosphere, and they affect the environment as well as human health. There are some existing methods available to analyze the lead (Pb^{2+}) and cadmium (Cd^{2+}) ions, such as atomic absorption spectroscopy [13], inductively coupled plasma atomic emission spectrometry [14], and inductively coupled plasma mass spectrometry [15]. These spectroscopic methods are expensive, time-consuming, and require specialized trained people and laboratories. Therefore, in this research work, a field effect transistor (FET) based active structure is used for the sensing platform [16]. The field effect transistor amplifies the strength of the input signal by the factor of the transconductance (g_m) of the amplifier. Channel is made up of rGO-L based sensing layer and is exposed to the target species. Gate to source voltage (V_{gs}) is varied from – 4 V to + 4 V at fixed drain to source voltage (V_{ds}) of 1 V, and input characteristics are plotted. Therefore, it is found that the sensor shows maximum response towards lead (Pb^{2+}) and cadmium (Cd^{2+}) ions at a gate voltage of – 1.6 V and 0.8 V.

II. EXPERIMENT

A. Synthesis of the Material:

The widely recognized modified Hummer's method is utilized for synthesizing graphene oxide (GO) sheets through the chemical exfoliation of graphitic powder [17]. Take 5 ml of the created GO and mix it with 100 ml of deionized water. Stir the mixture for 30 minutes. Lemon juice was extracted and filtered using a whatman filter paper. A volume of 15 ml of filtered juice was introduced into the solution, and the temperature was elevated to 80 ºC for a duration of 2 hours. Afterward, the solution was subjected to hydrothermal treatment for 24 hours at a temperature of 100 ºC. The solution turns a deep black color that indicates successful synthesis of rGO-L.

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B. *Characterization of Samples*

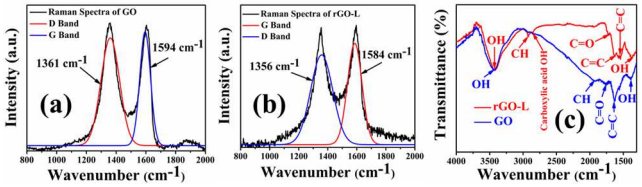

Figure 1 (a) Raman Spectra of GO (b) Raman Spectra of rGO-L (c) FTIR analysis of GO and rGO-L

Figure 1 (a) depicts the Raman analysis of the GO. It shows the D band at 1361 cm^{-1} and G band at 1594 cm^{-1} having the I_D/I_G of 0.84, and when it is reduced by the lemon juice, its D and G bands are shifted to lower wavenumber 1356 cm^{-1} and 1584 cm^{-1}, respectively as shown in figure 1(b). The I_D/I_G for rGO-L is 0.96, which is slightly increased than GO, indicating defect sights are increasing. FTIR analysis of GO and rGO-L is shown in the figure 1(c). The bending and stretching vibration of carboxylic acid, aliphatic ketone, and cyclic alkene is observed in the rGO-L compared to the graphene oxide, which affirms the reduction and attachments of functional groups in the rGO. The alteration of vibration frequency is due to the removal and attachment of different functional groups that come from the lemon juice.

C. *Device fabrication and Sensing setup*

A p+<100> type silicon wafer, doped with boron to have a resistivity of 0.001-0.005 ohm-cm, was employed as a substrate for device construction. A 120 nm layer of SiO_2 was formed by thermally oxidizing the wafer. A 10 nm titanium interlayer was used to improve the adhesion between gold and SiO_2. A layer of gold, with a thickness of 180 nm, was placed onto the titanium layer using DC sputtering. The gold and titanium layers underwent lithographic patterning to form source and drain electrodes, measuring 240 µm in width and with a channel gap of 40 µm. Due to the heavily doped wafer, a shadow mask was employed to fabricate the back gate. Schematics of the fabricated device with experimental setup and camera images are shown in figure 2.

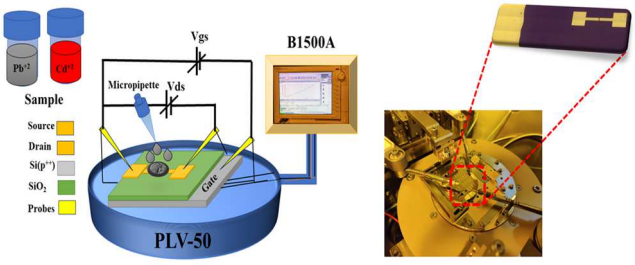

Figure 2 Schematic of the sensing device with experimental setup

III. Result and Discussion

Electrical characterization of the fabricated device is done with the help of PLV- 50 and B1500A semiconductor parameter analyzer. Transfer characteristics of the device that is drain to source current (I_{ds}) versus gate to source voltage (V_{gs}) show the ambipolar nature of graphene with the dirac point of -0.41 V as shown in figure 3 (a). This indicates defects are created on the surface. Hole currents are more than the electron current; therefore, this material is slightly p-type in nature. The output characteristics of the device ($I_{ds} - V_{ds}$) show that the device is normally on type depletion mode FET, having a current of 1 µA at the zero-gate voltage. The output current kept on increasing as the negatively biased gate voltage kept on increasing shown in the figure 3 (b).

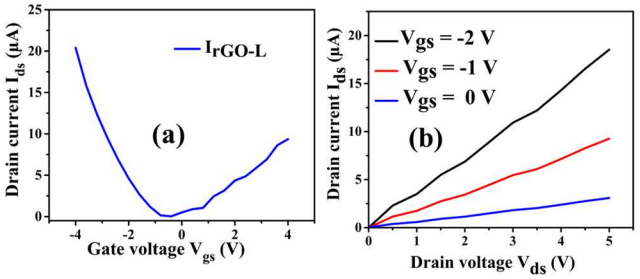

Figure 3 (a) Transfer characteristics of the device (b) Output characteristics of the device

The device is tested with five commonly present ions in water that are Na^+, K^+, As^{3+}, Pb^{2+}, and Cd^{2+} at zero gate voltage. It was found that the device shows a response towards lead (Pb^{2+}) and cadmium (Cd^{2+}) is 101.1 % and 93 %, and for the rest of the ions, it shows below 5 %, which is negligible at zero gate voltage as shown in figure 4.

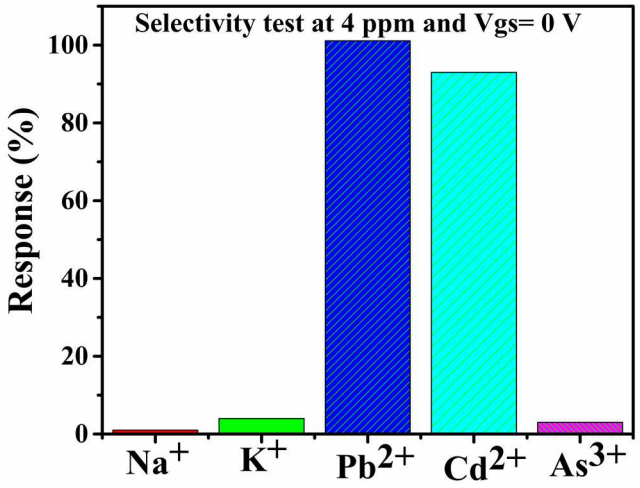

Figure 4 Selectivity test of the sensor at V_{gs} = 0 V

Therefore, the field effect is studied for lead (Pb^{2+}) and cadmium (Cd^{2+}) ions. The gate voltage ranges from -4 V to +4 V, while the drain to source voltage (V_{ds}) remains constant at 1 V. It has been shown that for Pb^{2+} ions, the current increases from 17 µA to 49.7 µA at a concentration of 4 ppm shown in figure 5(a). The current for Cd^{2+} increases from 20 µA to 40.6 µA when the concentration of Cd^{2+} is 4 ppm, as shown in figure 5(b)

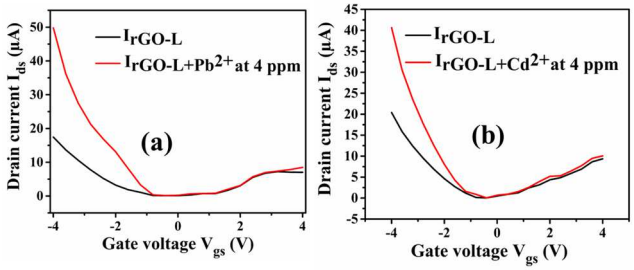

Figure 5 (a) Transfer characteristics of the device for Pb^{2+} (b) Transfer characteristics of the device for Cd^{2+}

Figures 6(a) and 6(b) depict the sensor's response to 4 ppm concentrations of Pb^{2+} and Cd^{2+} ions under different V_{gs} conditions at a fixed V_{ds} of 1 V. It was observed that the sensor exhibited the highest response to Pb^{2+} at -1.6 V and Cd^{2+} at 0.8 V. The device depicts the minimum current ranging from -1 V to 0.5 V V_{gs}. Thus, at this voltage range, there are incredibly few carriers present in the channel. Sensing response refers to the number of additional holes that are added to the existing holes in the channel. Therefore, the highest level of response is achieved within this range in the present research.

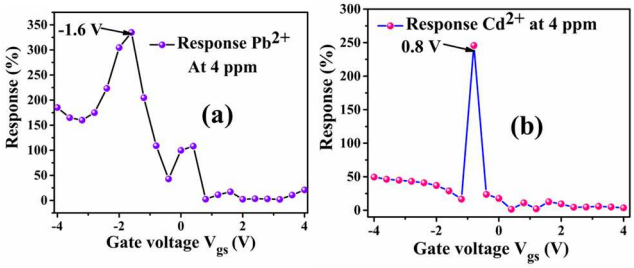

Figure 6 (a) Response of the device for Pb^{2+} at V_{ds} 1 V. (b) Response of the device for Cd^{2+} V_{ds} 1 V.

Figure 7(a) and 7(b) depict the output characteristics plot for Pb^{2+} and Cd^{2+} ions, respectively, for a different concentration ranging from 20 ppb to 80 ppb at an optimized gate voltage of -1.6 V and 0.8 V. Current I_{ds} increase as the amount of drop casted ions increased from 20 ppb to 80 ppb it shows the physisorption and chemisorption of Pb^{2+} and Cd^{2+} ions on the channel material at a V_{gs} of -1.6 V and 0.8 V respectively.

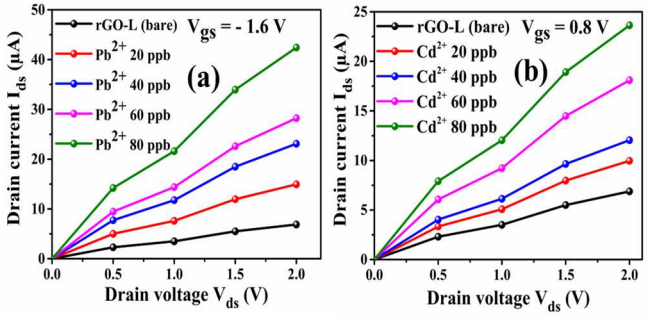

Figure 7 (a) I_{ds}-V_{ds} Plot for different Pb^{2+} ions. (b) I_{ds}-V_{ds} Plot for different Cd^{2+} ions.

The device's sensitivity was calculated, and it was found to be 0.75μA/ppb for Pb^{2+} and 0.4 μA/ppb for Cd^{2+}. The limit of detection (LOD) for Pb^{2+} and Cd^{2+} was 1 ppb and 2 ppb, respectively.

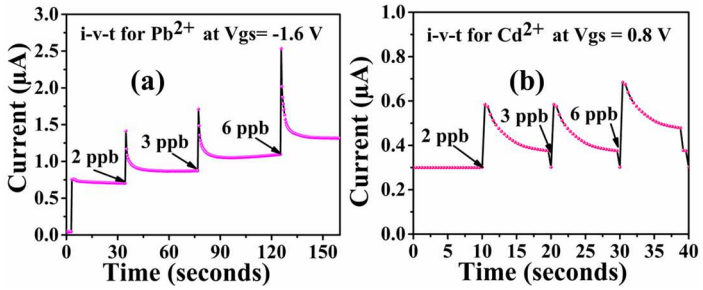

Figure 8 (a) Transient response for Pb^{2+} (b) Transient response for Cd^{2+}

Figure 8(a) and (b) show the transient response for Pb^{2+} and Cd^{2+} ions at a gate voltage of – 1.6 V and 0.8 V, respectively. Furthermore, it was found that the response time for Pb^{2+} was 20 seconds, and for Cd^{2+} it was 10 seconds.

IV. Proposed Sensing Mechanism

Reduced graphene oxide via lemon consists of oxygen-rich functional groups, i.e. OH, C=O. They have a high tendency to form a coordinate bond with Pb^{2+} and Cd^{2+} ions. According to hard and soft acid base theory (HSAB) [18], Pb^{2+} and Cd^{2+} are at the border of soft acids, and they prefer to bind with the borderline soft base that are the oxygen-containing functional groups present on the rGO-L surface. Whereas Na^{+} and K^{+} are hard acids, and they prefer hard base for the recombination. As^{3+} is a strong base and has different coordination, therefore not interacting with active sites present on the rGO-L surface. The sensor shows more response for Pb^{2+} as compared to Cd^{2+} because the ionic radius of Pb^{2+} is higher (approximately 119 pm) compared to that of Cd^{2+} (approximately 95 pm). Therefore, a large electronic radius allows it to interact with more oxygen-containing functional groups of rGO-L.

V. CONCLUSION

This research work exhibits the successful development of a reduced graphene oxide-based FET sensor, which uses lemon juice as a natural reducing agent and makes a material eco-friendly. The device is tested against five major toxic ions found in water, and cross-sensitivity is reduced by tuning the gate voltage. The resulting rGO-L sensor demonstrates the high selectivity towards the Pb^{2+} and Cd^{2+} ions at a gate voltage of -1.6 V and 0.8 V with detection range in ppb level making it suitable for the water health monitoring system application.

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